# SAFETY REQUIREMENTS AND HAZARDS IN MANUFACTURING OF CARBONACEOUS SMOKE PYROTECHNIC COMPOSITION.

## Dr. D.S.S. GANGULY, WORKS MANAGER ORDNANCE FACTORY KHAMARIA, JABALPUR, INDIA

#### **Summary**

Smoke composition are used in military warfares for various tactical roles. One of such screening composition has carbonaceous substance in form of pitch coal tar, along with sulphur, potassium nitrate, glue and Borax. The process of manufacture of composition involves making of pre-mix of vauious dry powder ingradients followed by slow addition of this premix to pre-melted pitch coal tar and glue in incorporator. The safety evaluation are made on the basis of the experimental data generation on this composition-by following conventional test methods like friction to direct mechanical shock, sensitiveness to friction temperature of Ignition, Behaviour of inflamation, chemical stability and environmental effects during manufacture.

This paper underlines the hazards involved and its safety requirements during manufacture of composition.

#### INTRODUCTION

The military use of smoke for screening and/or signalling is probably as old as warfare itself. Before, gunpowder and other pyrotechnic mixtures were available, smoke was made by the burning of natural material such as grass. The planned use of smoke in military operatons have developed during world war-I. During this period, smoke was used extensively for signalling, screening, troops movements and as a fear mechanism due to the ressemblance of screening smokes to certain toxic chemical agents. The tactical significance of the use of smoke, which was not fully realized untill the close of world war-I, was strongly considered early in world war-II where the requirements for smoke producing devices were much greater hence, the research and development programmes were established early during world war-II to obtain the information necessary to develop the tactically required smoke-producing items.

Modern military pyrotechnics as an out growth of "Greek fire" and the "Art of making fireworks" has progressed to the extent where pyrotechnic device and system in both offensive and defensive military operations have become indispensable. Pyrotechnic smokes are used for screening, flares, signals, colored and white smokes, tracers, incendaries and pyrotechnic delays.

1.1 Pyrotechnic munitions for producing smoke, whether for screening, signalling or other purposes are usually one of following general types:

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#### (a) Venturi Thermal generator type

The smoke producing material and the pyrotechnic fuel block required to volatilize the smoke material are in separate compartments. The smoke-producing material is atomized and vaporised in the venturi nozzles by the hot gases formed by the burning of the fuel block.

#### (b)Burning Type

Burning type smoke compositions are intimate mixtures of chemicals. Smoke is produced from these mixtures by either of two methods. In the first method, a product reacts with constituents of the atmosphere to form a smoke. In the second method, the heat of combustion of the pyrotechnic serves to volatize a component of the mixture which than condenses to form the smoke.

#### (c) Explosive dissemination type

The smoke -producing material is pulverized or atomized and than vaporized, or a reground solid is dispersed by the explosion of a bursting charge.

The ingradients used in smoke-producing chemicals and combustion products, and/or the condensed vapor particles produced in a smoke, should be considered to be irritating and/or toxic. Care should be exerted in working with smoke-producing materials and the resulting smokes, especially regarding the inhalation of high concentrations and long exposures thereto.

1.2 The screening smoke mixture consists mainly of fuels, oxidants, cooling agents and Binders.

#### (i) Fuels

The number of combustibles that are satisfactory in colored smoke mixture is very limited and includes, sulphur, thin-urea and sugars such as lactose, sucrose and dextrose. Black smoke are generally produced by burning of hydrocarbons such as phenanthrere, anthracene and pitch coal tar. The addition of anthracene or napthalene to high carbon, Smoke mixture also produces black smoke.

#### (ii) Oxidants

A large number of fuel -oxidant mixture have been investigated. The oxidizing agents studied includes chlorates, perchlorates, permanganate, nitrates, nitrites, peroxides and oxides.

#### (iii) Cooling agents

Cooling agents may be added to regulate the burning rate of the fuel and to lower the temperature sufficiently to prevent excessive decomposition of fuel with resultant decolorization or strong flamming e.g. NaHCo<sub>3</sub>, KHco<sub>3</sub>, Borax, Ammonium salts, kaolin etc.

#### (iv) Binders

Graphite, Zincoxide and linseed oil have been used as binders for binding the fuels, oxidants and cooling agents togather.

2.0 In our present study the following carbonaceous screening smoke compostion have been studied in details from the angle of its chemical behaviour, hazards involved and safety requirements during manufacture of the composition and filling in ammunition.

#### 2.1 <u>Ingradients of composition</u>

Pitch coal tar Glue Potassium Nitrate Sulphur Borax

The mixing of ingradients are in proportions/percentages. In the above composition pitch coal tar and sulphur acts as a fuel, potassium nitrates acts as an oxidant, Borax acts as a coolant, Glue acts as a binder. Besides, sulphur acts as a reducing agent and lowers ignition temperature of smoke.

#### 3.0 METHOD OF MANUFACTURE OF THE SMOKE COMPOSITION

The composition stated under (2.1), is manufactured as under:

The required amount of pitch and glue are charged in the incorporator (Fig.1) and the steam is turned on. The pitch used is melted and strained through wire mesh to get rid of any foreign matter before it is charged into incorporator.

When the pitch and glue is fully melted, the stirrer is rotated by hand to ascertain whether the blades move freely or not. Than the stirrer is started and continued for sometime to ensure complete homogenity of mixture. Subsequently the premix consisting of mixture of ground and sieved potassium nitrate, sulphur and borax is slowly added in small quantities at a time through the hopper into the molten mixture of pitch and glue and stirring continued for 2-3 hours. At the end when the mixture becomes completely hmogenous candles/smoke ammunition are filled by tapping from the bottom of the incorporator.

#### 4.0 BEHAVIOUR AND HAZARDS OF COMPOSITION

#### 4.1 Properties

(i) Sensitiveness to direct mechanical shock as determined by fall hammer apparatus with 2kg wt. and 20mg sample.

The figure of Insensitiveness-over 120 (Ref CE-70)

#### (ii) Nature of Explosion set up by shocks-Not violent.

The figure of insensitiveness expresses the relative amount of energy necessary to produce explosion in a small quantity of explosive subjected to direct blow between hard surfaces, picric acid (100) is taken as the standard. A figure of 90 or above denotes an explosive which is fairly safe from this point of view. A figure of 40 or below denotes a sensitive explosive which should be handled with considerable caution.

#### (iii) Sensitive to friction

A small quantity of explosive is laid on a flat surface and struck with amallet in such a manner that it receives a flaming blow. The figure indicates the percentage of ignition abtained in 10 tests.

Nature of Mallet- stone Anvil, Hard wood, Anvil, Teak wood

#### (iv) <u>Temperature</u> of <u>ignition</u>

More than 350°c.

The Temperature of ignition is determined by gradually raising the temperature of a small quantity of explosive at the rate of 5°c per minute and noting when ignition occurs, it should be noted that ignition may occur at lower temperatures if the explosive is heated up more slowly.

#### (v) Inflamability

Three grams of explosive are introduced into a glass tube 5/8 inch in dia, gently shaken down and subjected to the flash from a piece of Bickford fuze resting vertically on the surface. Under these conditions, the explosive - FAILS TO IGNITE.

#### (vi) Behaviour of inf lamation

When placed loosely in an iron trough of Semi -circular section, 1/2 inch in dia and 12 incheg long and ignited by a flame, the explosive-The material gets ignited with difficulty but burns steadily when lit.

#### (vii) Chemical stability- satisfactory.

(viii) Special precautions should be taken to prevent this explosive coming into contact with the following substances except in authorised mixtures and under regulated conditions-chlorates, High explosives, propellants, Nitro bodies, phosphorous, copper and its alloys.

#### (ix) Poisonous ingradients

Prolonged and intimate contact with pitch may be injurious to health.

### 5.0 SAFETY REOUIREMENTS DURING MANUFACTURE OF COMPOSITION AND USE

- 5.1 The composition after manufacture is comparatively safe to handle and requires only the normal precautions applicable to explosives generally. Tools made of copper and its alloys should be avoided.
- 5.2 Since, the composition is likely to get ignited during manufacture, the following safety measures should be taken during manufacture.
- 5.3 The composition making for discussions can be divided into following steps.
- (a) Grinding of pre-mix ingradients, mixing and storage.
- (b) Melting of pitch and glue in incorporators.
- (c) Addition of premix to molten pitch coal tar and glue in incorporator.
- (d) Incorporation of mixture.
- (e) Filling of composition in smoke candles/Ammunition.
- (a) Grinding of premix ingradients, mixing and storage.
- (i) The ingradients should be free from impurities other than specified including foreign particles. (iron pieces, mud, stone etc.). If required magnetic separators can be employed. The ingradients of premix should be properly ground and sieved.
- (ii) The ingradients after grinding should be dried in oven as moisture is undesirable element.
- (iii) The pre-mix of potassium nitrate, sulphur and Borax should be thoroughly mixed by hand.
- (iv) The pre-mix mixture should be stored out of hummidity, as it is hygroscopic in nature and caking takes place. This lumps creates hazards during mixing in incorporators. Also, it creates non-homogenity in composition, resulting in flaming and non uniform generation of smoke during use.
- (v) The pre-mix composition should not come in contact with any part of the body. Grinding

of ingradients should be remote controlled and hand mixing be carried out with hand gloves. Never do mechanical mixing as it may lead to fires.

- (vi) Copper trays should be avoided for keeping the premix. The pre-mix should be properly covered from ingauss of moisture during storage. The premix should be prepared on day to day basis.
- (vii) It is desirable to add sulphur after addition of other ingradients in pre-mix.
- (b) Melting of pitch coal tar and glue
- (i) Melting of pitch coal tar should be carried out in separate incorporators, first to remove extra oil and than the molten mass should pass through sieve/wire mesh to remove solid foreign particles. Than it should be cast, dried, broken and added to main incorporator for making of smoke pyrotechnic composition.
- (ii) The temperature of pitch coal in incorporator should not go beyond  $120^{\circ}$ c.
- (iii) The glue should be free from impurities.
- (iv) The sieved, dried, crushed pitch coal tar and glue should be added to main incorporator. The steam should be gradually raised so that the pitch coal tar and glue completely melts. Once the pitch coal tar and glue have completely melted than only start the blades of incorporator-(Fig 2). First by hand the shaft should be rotated to see its free movement and than only the stirrer motor to be put on or else, the big lumps of unmelted pitch coal tar will creat friction/damage to the blades of stirrer-( The process as discussed under-3.0)
- (v) After the stirrer is put on wait for 2-3 hours for thorough mixing of ingradients or else it will not give required end results on ignition.
- (c) Addition of pre-mix to molten pitch and glue for incorporation.
- (i) The separately prepared pre-mix (5.1) is slowly added through the hopper (Fig-3) in the lid of the incorporators @500 gms per minute, addition should be uniform in quantity through each hoppers. Measured aluminium containers can be used for additions. Steam regulator should be controlled to see that the temperature of mixture does not rise above 120° c. If the addition is not uniform than hot pockets may be created which creates spurting and bursting of smoke containers and in extreme cases flaming in use. Also, it is hazardous during manufacture as it catches fire.
- (ii) After completion of addition of premix stir for another one hour with uniform speed of stirrer and temperature.
- (d) Filling of composition in candleslAmmunition

This ready composition is tapped from bottom of incorporator (Fig 1) and filled in candles at a stretch to avoid air gaps. These air gaps leads to bursting of containers on ignition.

#### 6.0 MAINTAINANCE OF INCORPORATOR

- 6.1 The incorporator should be periodically maintained, cleaned to check regarding broken bolts and foreign perticles. Loose fitting of stirrer to shaft creates friction during incorporation leading to fire.
- 6.2 The motor and electrical parts should be checked for flame proof.
- 6.3 Automatic drenching system should be over the incorporators.

#### 7.0 PERSONNEL SAFETY

Besides, general safety, it is essential to provide an efficient system to remove the fumes arising during melting and incorporation. Also, the persons working in this area should wear safety protective breathing apparatus.

#### 8.0 FIRE FIGHTING /EXTINGUSHERS

- 8.1 Probable causes of fire during stages of manufacturing has been dealt under (5.0), it can be seen that the fire can broadly be initiated due to
- (i) Friction of metallic parts during mixing in incorporators.
- (ii) Due to rise of temperature of the composition during mixing.
- (iii) Initiation of fire by spark/electricity conveyed from the motor.
- (iv) Improper following of safety measures dealt under (5.0) above.

#### 8.2 Fire extinguishers

It is stressed that so far no extinguishers are existing which can extinguish the fire once the fire catches in the incorporator during manufacture of composition and filling. The spread of fire is also very rapid due to presence of inherent oxidising agent in the mixture.

At the most the cooling of plant, machineries and installations can be carried out by drenching with water or spraying water. Also, the thick black smoke in building during fire screens the fire fighting persons from fire-fighting.

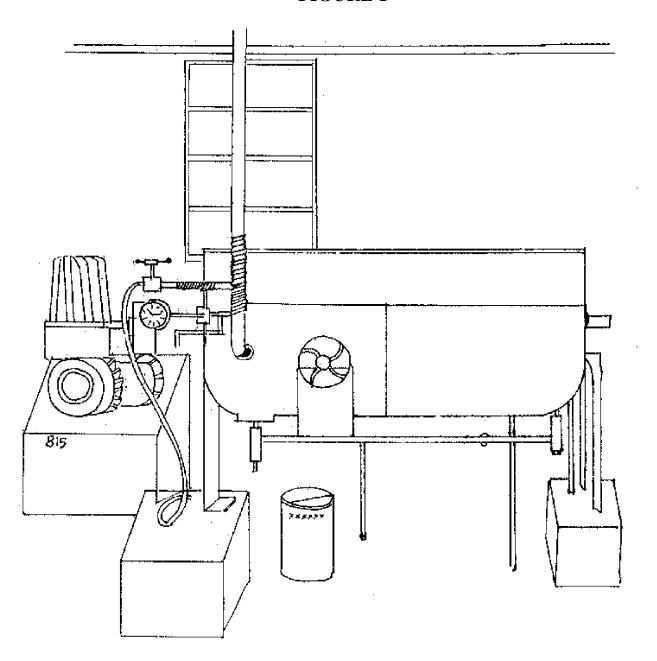
#### 9.0 CONCLUSIONS

The carbonceous smoke composition involving pitch coal tar, sulphur, glue, potassium Nirtate and Borax is comparatively safe to handle, transportation and gives satisfactory performance to the user. But, its manufacture involves safety measures of highest order as stated in this paper. Any deviations leads to hazards and the most important part is that no extinguishers are available on date which will extinguish the fire once initiated during manufacture. Only quenching by water helps stopping of spread of fire and to some extent loss to installations.

#### References

AMC pamplet - Engineering Design Handbook -Military pyrotechnics Series part one - Theory and Applications. (Head Quarters, U.S. Army Material Command April 1967).

FIGURE 1



### FIGURE 2

